



Concentrated sulfonated poly (ether sulfone)s as proton exchange membranes

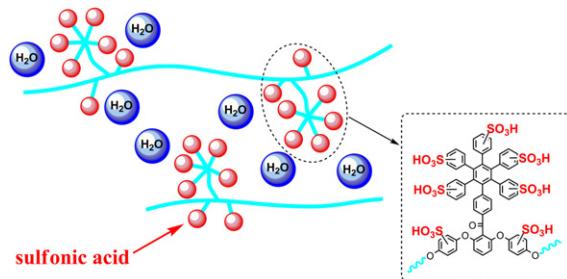
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HIGHLIGHTS

- A series of new concentrated sulfonated poly (ether sulfone)s were synthesized.
- These polymers own lower activation energy (E_a) of conductivity compared to Nafion.
- The membrane with IEC = 1.66 mequiv g⁻¹ exhibits higher conductivity than Nafion.
- These membranes show considerable water management and proton conductivity.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel bisphenol monomer containing concentrated electron rich phenyls is synthesized, which provides a locally and densely postsulfonation sites. Based on this monomer, a series of new sulfonated poly (ether sulfone)s (SPESs) are successfully obtained by nucleophilic substitution reaction, followed by postsulfonation using concentrated sulfuric acid. All the polymer membranes are readily prepared by solvent casting and exhibit excellent thermal stability and mechanical properties. As ion exchange capacity (IEC) ranging from 0.98 to 1.66 mequiv g⁻¹, the polymers afford considerable proton conductivity and water absorption. SPES-3 with IEC = 1.66 mequiv g⁻¹ shows equal proton conductivity (0.131 S cm⁻¹) to Nafion 117 at 100 °C under fully hydrated state. At low IEC level (IEC = 0.92 mequiv g⁻¹), SPES-1 also exhibits higher conductivity (>10⁻² S cm⁻¹) than some earlier reported sulfonated random polymers. Their excellent performance is attributed to the internal structure of the polymers, which formed distinct phase separation between hydrophilic and hydrophobic moiety observed by SAXS. A combination of high proton conductivities, moderate water uptake, suitable mechanical properties and low swelling ratios for some of the obtained SPES indicates that they are good candidate materials for proton exchange membranes (PEMs).

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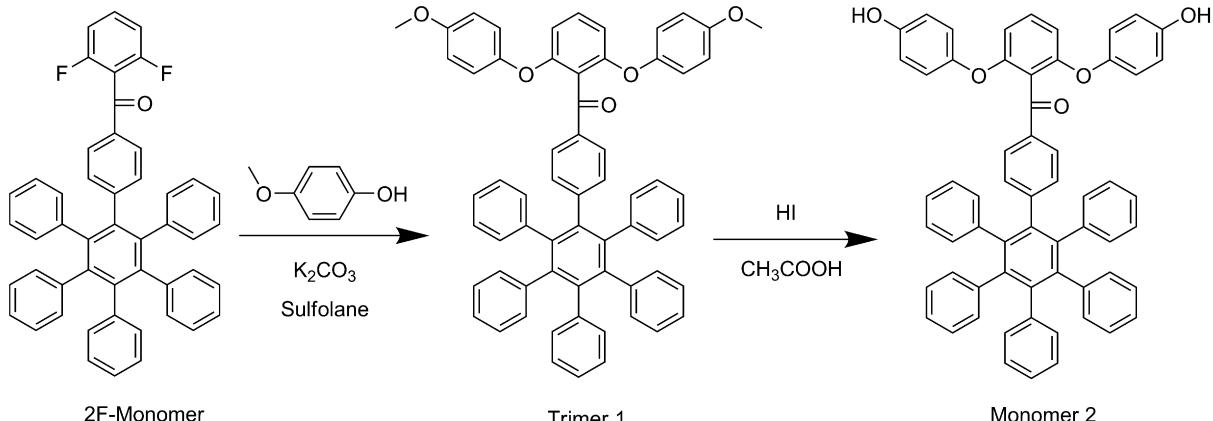
1. Introduction

Proton exchange membranes fuel cells (PEMFCs), regarding as a significant efficient and renewable energy resource, have attracted more and more attention in recent years. The advantages of fuel cells are their high efficiency and power/energy density, low temperature operation, rapid start-up time [1,2]. Proton exchange

membrane (PEM) is a critical part in PEMFC, which serves as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport [3]. The perfluorosulfonic acid ionomer membranes, represented by Nafion (a registered trademark of DuPont Co.), are the most commonly used PEMs and have acted as benchmarks for membrane performances due to their excellent chemical and electrochemical stabilities as well as outstanding proton conductivity [4,5]. However, the cost of Nafion remains high because the polymerization process of perfluorinated polymer is complex and must be carried out under harsh conditions such as high temperature and high pressure [6–8]. Moreover, the

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Scheme 1. Synthesis of monomer 2.

mechanical stability and proton conductivity of Nafion can decrease when it is heated over 80 °C, owing to its low glass transition temperature [9,10].

Hence, many arduous efforts are made to exploit an alternative material for PEM. Sulfonated aromatic polymers are supposed to be the most promising candidate for Nafion, considering their well-known oxidative, hydrolytic stability under harsh conditions and many different chemical structures [8]. Despite these advantages, this series of polymer also faces many issues need to be worked out. It is envisaged that the proton conductivities of randomly sulfonated ionomers are too low as compared with Nafion at the same ionic exchange capacity (IEC) level. While higher IEC value results in excessive water content, which is beneficial for proton transportation but a disaster for mechanical property, dimensional stability and durability. And most random SPAE-type membranes formed ambiguously phase-separated microstructures because of their rigid molecular chains and weak hydrophilic/hydrophobic nature [11–14].

Therefore, we should precisely control the position and density of sulfonic acid groups to form well-connected channels for the transportation of hydrated protons [15], and avoid excessive water uptake happens at the same time. Recently, densely sulfonated copolymers have been attracting increasing attention because of the high contrast in polarity between the hydrophilic and hydrophobic units, this promotes the formation of hydrophilic–hydrophobic phase-separated structures [16]. These polymers contain fewer hydrophilic segments at the same level of IEC values with normal sulfonated ones, and relatively more hydrophobic segments endows them good dimensional stability and mechanical properties. Earlier, Ueda et al. reported novel locally and densely sulfonated poly(ether sulfone)s prepared for PEM. These PESS owned efficient proton conduction in a wide range of 30–95% RH at 80 °C, which were comparable with that of Nafion [17]. Hay and co-workers synthesized dendritic multiblock copoly(ether sulfone)s, bearing sulfonated dendritic clusters, that afforded desirable proton conductivity at a level of IEC (0.92–1.26 mequiv g⁻¹) similar to Nafion [18]. It was expected that the large difference in polarity between the densely sulfonated, hydrophilic portions and the hydrophobic portions of the polymer would produce a greater degree of microphase separation, which in turn would lead to well-developed hydrophilic channels and higher proton conduction. While these densely sulfonated polymers were less studied since the complicated monomers were not easy to tailored and synthesized. Additionally, there was little research on how the distribution of concentrated sulfonic acid groups and the density of them influence internal morphology and even conductivity.

Herein, we design a new monomer containing concentrated phenyls pendent group. To make an approach to the formation of water channels in PEM, a series of sulfonated aromatic polymer are obtained based on the new monomer. The densely sulfonic acid groups on pendent chains are expected to aggregate and form continuous hydrophilic domains, which enhances the phase separation between hydrophobic main chain and hydrophilic side chain. Additionally, aromatic backbone architecture endows polymer with superior thermal and mechanical stability. In this study, we aimed at whether concentrated sulfonic groups on pendent chains would be beneficial for proton conduction and dimensional stability. To investigate the detailed property of this polymer, some measurements were implemented and further discussions will be carried out later.

2. Experimental

2.1. Materials

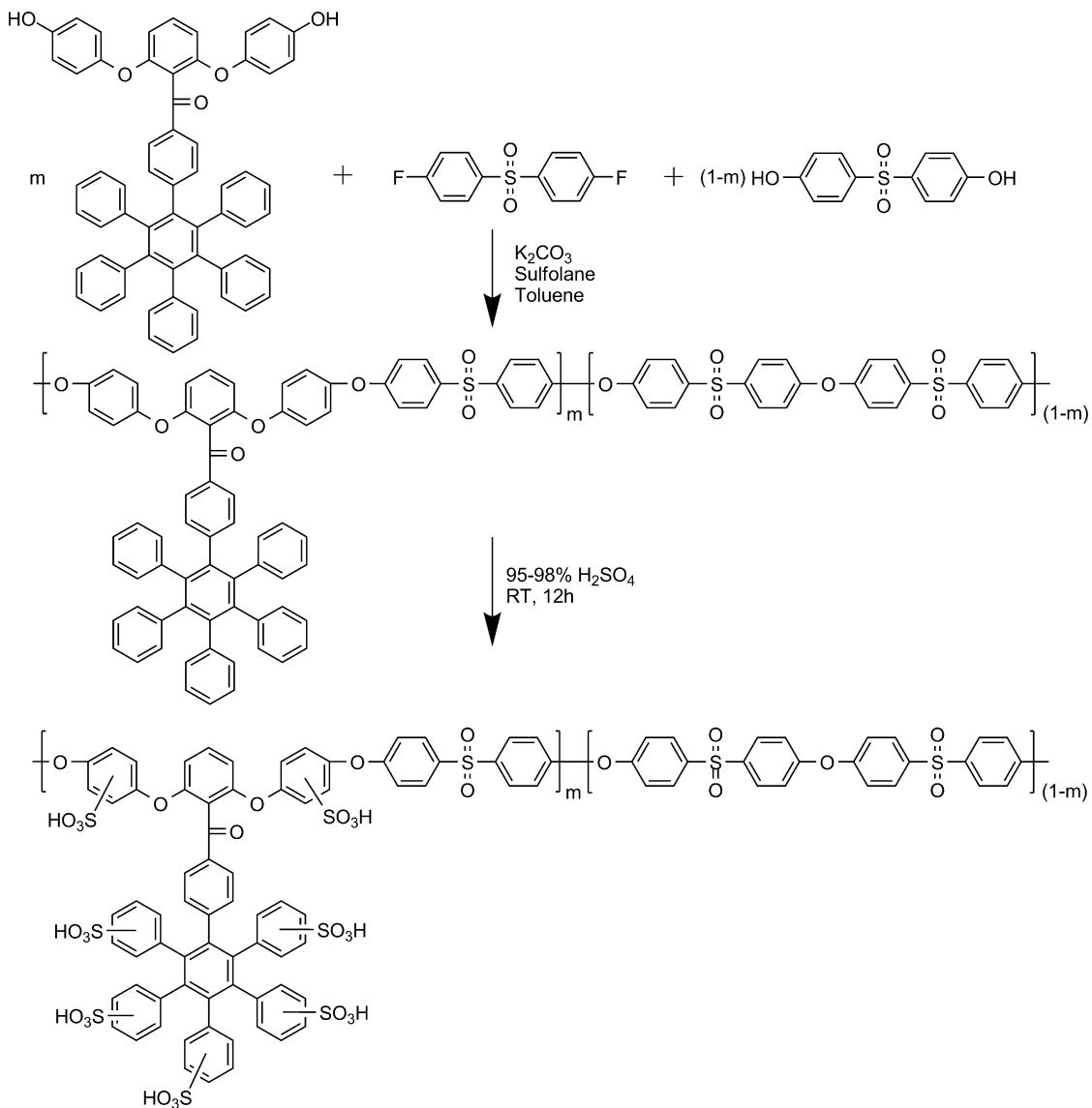
4,4'-Difluorodiphenyl sulfone (DFDPS) and 4,4'-dihydroxydiphenyl sulfone (DHDPS) was purchased from Japan Chemical Industries, Ltd. DHDPS was purified by recrystallization from deionized water. Sulfolane was purified by vacuum distillation. Anhydrous potassium carbonate was dried at 120 °C for 24 h before used. 2,6-Difluoro-4'-(2,3,4,5,6-pentaphenyl phenyl) benzophenone (2F-monomer) was synthesized in our laboratory via several steps. All other organic solvents were obtained from commercial sources and purified by conventional methods.

2.2. Synthesis

The synthetic processes of monomers and polymers are depicted in Schemes 1 and 2 respectively.

2.2.1. Synthesis of trimer 1

To a 50 mL round-bottom three-necked flask equipped with a mechanical stirrer and a Dean–Stark trap, 2F-monomer (6.748 g, 0.01 mol), 4-methoxyphenol (3.104 g, 0.025 mol) and anhydrous potassium carbonate (3.869 g, 0.028 mol) were charged. Afterward, 30 mL of sulfolane and 5 mL of toluene were added into the flask under argon. The reaction was initially carried out at 140 °C for 3 h to remove the water completely. The subsequent polymerization was performed at 210 °C for 6 h. Then the reaction mixture was poured into water, washed with 15% NaOH (aq) and distilled water several times. The crude product was recrystallized from toluene. Mp: 248.2 °C. Mass spectrum (*m/z*): 883.4 (100% relative



Scheme 2. Synthesis of polymers.

abundance). 1H NMR (500 MHz, $DMSO-d_6$, δ): 3.75 (s, 6H, OCH_3), 6.38–7.35 (m, 40H, Ar H).

2.2.2. Synthesis of monomer 2

Trimer 1 (3.53 g, 4 mmol), 5.3 mL of HI (57 wt.% aqueous solution) and 100 mL of acetic acid were added into a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The mixture was heated to reflux under argon for 6 h to give a purplish red solution. After cooling to room temperature, the solution was poured into water. The mixture was filtered to provide a pink filter cake, which was washed with distilled water for several times. Recrystallization of the crude product from toluene afforded monomer 2 in 90% yield as a white powder. Mp: 257 °C. 1H NMR (500 MHz, $DMSO-d_6$, δ): 9.1–9.4 (s, 2H, OH), 6.38–7.35 (m, 40H, Ar H).

2.2.3. Synthesis of poly(ether sulfone)-3 (PES-3)

Into a 50 mL three-necked round-bottom flask equipped with a mechanical stirrer, a Dean–Stark trap, an argon inlet/outlet and a reflux condenser, monomer 2 (0.547 g, 0.64 mmol), DHDPS

(0.841 g, 3.36 mmol), DFDPS (1.017 g, 4 mmol) and K_2CO_3 (0.607 g, 4.4 mmol) were charged. Additionally 6 mL of sulfolane and 10 mL of toluene were added into the flask. The mixture was heated to 140 °C in an oil bath for 3 h. After dehydration and removal of toluene, the reaction temperature was increased to 200 °C. After 6 h, the mixture was slowly poured into water. The resulting fiber was filtered and washed with distilled water and hot ethanol several times. The polymer was dried in vacuo at 120 °C for 12 h. PES-1 and PES-2 were synthesized in a similar way as described above, and it's needless to repeat here.

2.2.4. Sulfonation of copolymer

A common sulfonation method of the polymer was described as follows. 1 g of dried polymer was added into a round-bottom flask equipped with a magnetic stirrer. Afterward, 10 mL of concentrated sulfuric acid was poured into the flask. The mixture was stirred at room temperature for 12 h. Then the purplish solution was slowly poured into ice water with stirring. The resulting pink fiber was filtered and washed with distilled water to neutral. The sulfonated polymer was dried in vacuo at 120 °C to give dark purplish solid.

2.2.5. Preparation of polymer membrane

A *N,N*-dimethyl acetylamide (DMAc) solution of a sulfonated polymer was filtered and cast onto a flat glass plate. The film was heated at 60 °C for 3 h, 80 °C for 3 h, 100 °C for 3 h, and 120 °C for 1 h. Then the film was dried in vacuo at 120 °C for 12 h. The dried film was immersed in 2 M H₂SO₄ (aq) at room temperature for 24 h and then thoroughly washed with water at 80 °C to give a tough, flexible and transparent membrane with a thickness in the range of 60–80 μm.

2.3. Characterizations

¹H NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz for ¹H) using DMSO-d₆ as solvent. Tetramethylsilane (TMS) was used as an internal standard. FT-IR spectra (film) were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument. Thermogravimetric analysis (TGA) was employed to assess thermal stability of membranes with Pyris 1 TGA (Perkin–Elmer) under a nitrogen atmosphere. Before analysis, the films were dried and kept in the TGA furnace at 100 °C in a nitrogen atmosphere for 15 min. The samples were cooled to 80 °C and then reheated to 800 °C at 10 °C min⁻¹, and the temperatures at 5% weight loss were recorded for each sample.

2.3.1. Water uptake and swelling ratio measurements

A piece of film was vacuum dried at 100 °C to a constant weight, which was recorded as W_{dry} and then immersed in deionized water at different temperatures. During this period, the wet membrane was quickly weighed several times after removing the surface water with tissue paper until a constant weight was obtained, which was recorded as W_{wet} . The water uptake was reported using water weight percent of dry membranes as following relation:

$$\text{water uptake}(\%) = \left[\left(W_{\text{wet}} - W_{\text{dry}} \right) / W_{\text{dry}} \right] \times 100\%$$

The in-plane swelling ratio was calculated from the change of film length by

$$\text{swelling ratio}(\%) = \left[\left(L_{\text{wet}} - L_{\text{dry}} \right) / L_{\text{dry}} \right] \times 100\%$$

where L_{wet} and L_{dry} are the lengths of the wet and dry membranes, respectively.

The hydration numbers (λ), the numbers of water molecules absorbed per sulfonic acid, were calculated according to the equation

$$\lambda(\text{H}_2\text{O}/\text{SO}_3\text{H}) = \left\{ \left(W_{\text{wet}} - W_{\text{dry}} \right) / M_{\text{H}_2\text{O}} \right\} / \left\{ (\text{IEC}/1000) \times W_{\text{dry}} \right\}$$

where $M_{\text{H}_2\text{O}}$ is the molecular weight of water.

2.3.2. Ion-exchange capacity (IEC) of the membranes

The IEC values of the membranes were determined by classical titration. Membrane samples (about 0.09 g) were immersed in 2 M NaCl solution for at least 24 h to liberate the H⁺ ions (the H⁺ ions in the membranes were replaced by Na⁺ ions). The exchanged protons within the solutions were titrated with 6 mM NaOH aqueous solution by using phenolphthalein as an indicator. For each sample, at least three measurements were carried out until the titration reached to a constant value. The IEC value was calculated from the titration result via the following formula:

$$\text{IEC} \left(\text{mequiv g}^{-1} \right) = V_{\text{NaOH}} \times C_{\text{NaOH}} / W_{\text{dry}}$$

where V_{NaOH} was consumed volume of NaOH, C_{NaOH} was molarity of NaOH, and W_{dry} was the weight of dry membranes.

2.3.3. Proton conductivity

Proton conductivity measurements were conducted on a Solartron 1260/1287 impedance analyzer by a four-electrode ac impedance method over a frequency range of 10–10⁶ Hz with 50–500 mV oscillating voltage. A sheet of the sulfonated membrane (3 × 1 cm) was placed in a test cell. Before the measurements, the membranes were fully hydrated in water at different temperatures for 48 h. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water at the desired temperature. The conductivity (σ) of the membranes in the transverse direction is calculated from the following equation:

$$\sigma = D / (RA)$$

where D is the distance between the two electrodes. R and A are the measured resistance and transverse area of the film samples, respectively.

2.3.4. Oxidative stability

A small piece of the membrane sample is soaked in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C. The oxidative stability is evaluated by recording the time when the membranes disappear and the retained weights of membranes after treating in Fenton's reagent for 2 h.

2.3.5. Mechanical properties of membranes

The mechanical properties of wet membranes were measured at room temperature on SHIMADZU AG-I 1 KN at a strain rate of 2 mm min⁻¹. The size of samples was 20 × 4 mm. The samples in wet state were obtained by immersing them in water for at least 48 h.

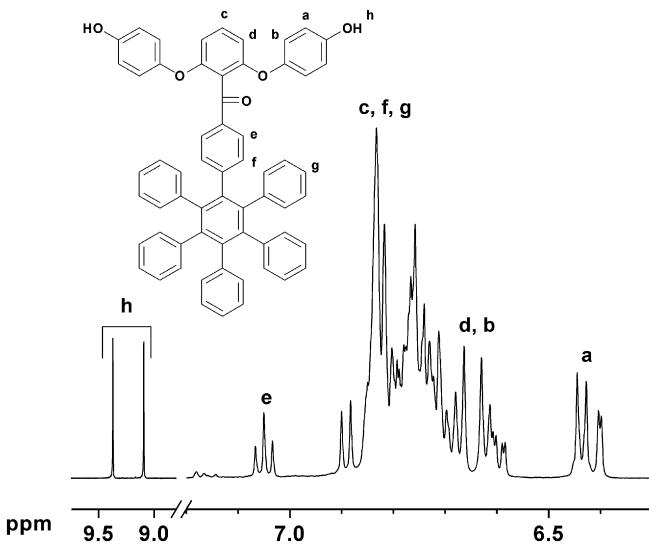
2.3.6. Morphological analysis

Small angle X-ray scattering (SAXS, Rigaku D/MAX 2550) was measured for membranes at room temperature. The membranes were enveloped in a Mylar bag and irradiated by X-ray (CuK α , $\lambda_i = 1.54 \text{ \AA}$) with 40 kV. The range of scattering vectors explored ($q = 4\pi\sin 2\theta/\lambda_i$) was from 0.08 to 3.0 nm⁻¹, where λ_i and 2θ are the incident wavelength and total scattering angle, respectively. And domain periodicities (d) were calculated from Gaussian fits to the principal scattering maxima of the Lorentz-corrected intensities using $d = 2\pi/q$.

3. Results and discussions

3.1. Synthesis of monomer

As shown in Scheme 1, a new monomer 2 containing highly concentrated sulfonation sites was successfully synthesized. The synthesis route started with self-synthesized 2F-monomer. Trimer 1 was obtained by the nucleophilic reaction of 4-methoxyphenol with 2F-monomer. Monomer 2 was obtained by the demethylation of 1 using HI. To characterize the obtained compound, ¹H NMR, IR, DSC and MALDI-TOFMS were carried out. The ¹H NMR spectrum of monomer 2 is shown in Fig. 1. The singlet peaks at 9.1 and 9.4 ppm were assigned to hydroxyl protons (H_h), and signals located about 6.4 ppm were assigned to the H_a , while those overlapped peaks around 6.6–7.2 ppm were assigned to the pendent phenyls group of monomer 2.

Fig. 1. ^1H NMR spectrum of monomer 2.

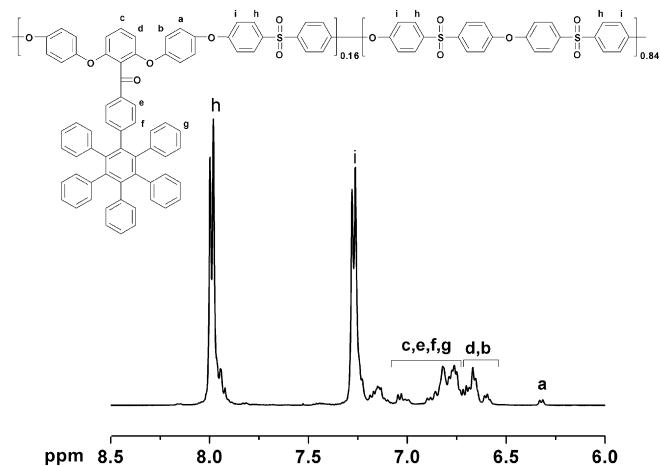
3.2. Synthesis of polymers

Poly(ether sulfone) was selected as the main chain because of its high adaptability to PEM applications. To build hydrophobic units, DFDPS and DHDPS were used as comonomers since their phenyls are deactivated by sulfone group in sulfonation reaction. Random copolymers were synthesized via nucleophilic polycondensation from DFDPS, DHDPS and monomer 2 (shown in Scheme 2). The feed ratio of monomer 2 to DHDPS was changed to get polymers with different IEC values after sulfonation (shown in Table 1).

The ^1H NMR spectrum of polymer PES-3 is shown in Fig. 2. All signals were well assigned, and the expected copolymer structure was confirmed. The integral ratio of the peaks at 7.28, 7.96 and 6.6–7.2 ppm, which were assigned to the H_i , H_h and (a, b, c, d, e, f, g) protons, respectively, was calculated to determine the polymer composition. The calculated composition from the ^1H NMR spectrum was $H_i:H_h:(a, b, c, d, e, f, g) = 7.36:7.36:6.67$, and based on these values we determined $m = 0.166$, which matched well with the feed ratio (monomer 2:DHDPS = 16:84).

3.3. Sulfonation of the polymers

It is well-known that sulfonation is an electrophilic reaction and the substitution sites of $-\text{SO}_3\text{H}$ groups are often determined by the substituents of benzene rings. According to some earlier reports [19], pendent benzene rings without substituents or with electron-donating substituents, such as methyl and phenyl, favored the sulfonation. As shown in Scheme 2, sulfonation of polymer was

Fig. 2. ^1H NMR spectrum of PES-3.

carried out by using concentrated sulfuric acid. The sulfonated polymers were readily soluble in polar aprotic solvents such as DMF, DMAc, and DMSO.

^1H NMR and FT-IR spectra were often used to confirm the structure of sulfonated polymers. In ^1H NMR spectrum of SPES-3 (Fig. 3), after the introduction of sulfonic acid groups, the signals at 6.6–7.2 ppm decreased and signals assigned to the g' protons, which were neighbors of the sulfonic acid groups, appeared at around 8 ppm. In FT-IR spectrum (Fig. 4), a new absorption peak occurs at 1036 cm^{-1} after sulfonation, which corresponds to the asymmetric vibration of $\text{O}=\text{S}=\text{O}$ in sulfonic acid group. The band at 1640 cm^{-1} corresponding to stretching vibrations of the diphenylcarbonyl segments was also observed in the spectra of SPESS. Both ^1H NMR and FT-IR results indicated the successful introduction of sulfonic acid groups. The IEC values of SPESS were determined by titration and agreed well with the calculated values (Table 1). This result indicates that selective and complete sulfonation to the monomer 2 moiety was achieved.

3.4. Water uptake and swelling ratio

Water uptake of membranes is an important factor for proton conductivity because water molecules play a vital role as proton transportation carriers in membranes. But excessive water content leads to dimensional instability, decrease in mechanical property

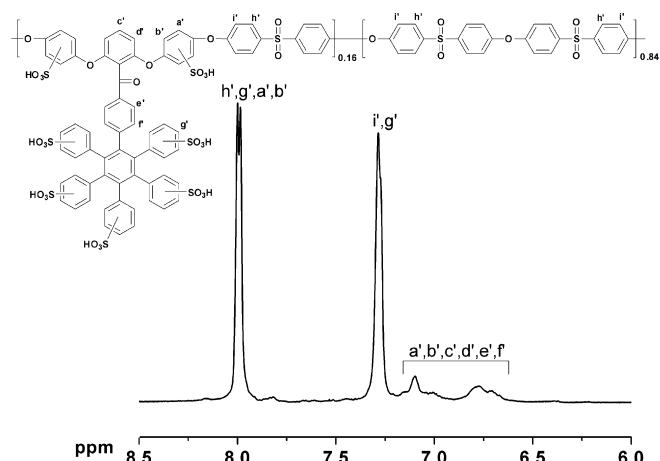
Fig. 3. ^1H NMR spectrum of SPES-3.

Table 1
Some properties of polymer.

Sample	Monomer 2 content (%) ^a	IEC ^b (mequiv g ⁻¹)	IEC by titration ^c	$\sigma(\text{S cm}^{-1})$		$T_{d5\%}$ (°C)
				20 °C	100 °C	
SPES-1	8	0.98	0.90	0.0224	0.0569	403
SPES-2	12	1.35	1.27	0.0424	0.1011	400
SPES-3	16	1.66	1.51	0.0631	0.1314	395
Nafion 117	—	0.90	—	0.053	0.137	—

^a Molar ratio of monomer 2 in the hydroxyl groups containing monomers.

^b Theoretical IEC value.

^c Determined by titration with 0.006 M NaOH (aq).

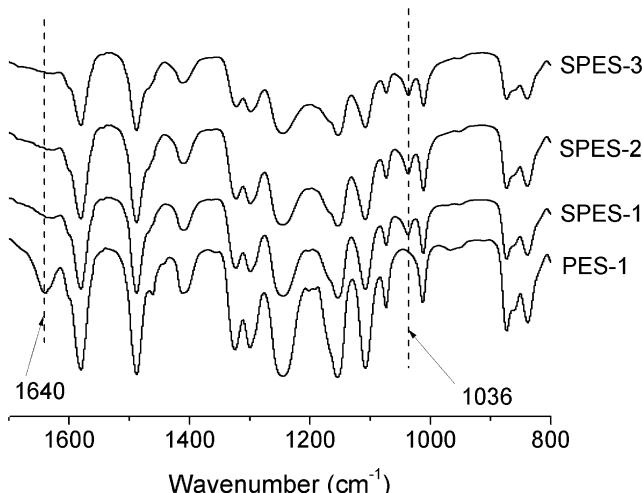


Fig. 4. Normalized FT-IR spectra of PES-1 and SPES-1, 2, 3.

and insufficient durability. Depending on IEC, polymers bearing more ionic groups have higher water content under the same condition. As temperature varies from 20 °C to 100 °C, the water uptake and swelling of membranes only have a slighter increase (Fig. 5). These properties were distinct from some early reports [20–23] of sulfonated random polymer with similar IECs, which always have an extraordinary raise of water uptake at higher temperature. Without dramatic increase in water content and dimensional change, the membranes were kept away from physical degradation. It's believed that concentrated sulfonic acid groups improve the water management in these sulfonated random polymers. Moreover, hydration numbers (λ) of SPESs were calculated and listed in Table 2, and they seem related to IEC values and temperature. SPES-2 and SPES-3 have higher λ than Nafion, thus it's assumed that more water molecules gathered around enhance the dissociation of the hydrophilic sulfonate groups, resulting in higher

proton conductivity. However, further attempt to superior water management are willing to be undertaken, seeing that Nafion performs more efficiently proton conductivity with less water.

3.5. Proton conductivity

As illustrated in Fig. 6, proton conductivities for the membranes with different IECs were measured as functions of temperature under fully hydrated state (in water). Apparently, with IEC values ranging from 0.98 to 1.66 mequiv g⁻¹, proton conductivity increases from 0.022 to 0.063 S cm⁻¹ at room temperature (Table 1). For a certain IEC value, the proton conductivity shows the same trend when temperature changes, and an elevated temperature turns it more efficient due to the enhanced charge transport. Compared with Nafion, SPES-2 and SPES-3 exhibited comparable conductivity over the entire temperature tested, since they have higher IEC values 1.35 and 1.66 mequiv g⁻¹, respectively. SPES-3 performed better indeed at 100 °C, and a higher conductivity (0.131 S cm⁻¹) is desirable for sulfonated aromatic random polymers. Owning a similar IEC value with Nafion, SPES-1 exhibited higher conductivity ($>10^{-2}$ S cm⁻¹) than some earlier reported sulfonated random polymers [20–23]. And higher IEC values (>1.2 mequiv g⁻¹) were required for these polymers, which afforded comparable conductivity of SPES-1 raised from 0.02 to 0.06 S cm⁻¹. The activation energy (E_a) of conductivity is calculated by fitting the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/RT)$. Curves are fitted linearly for E_a determination. The apparent activation energy of SPES-1 for proton conduction was estimated to be about 10 kJ mol⁻¹ from the asymptotic slope at 20–100 °C, close to that of Nafion 117 (9.7 kJ mol⁻¹). Attributed to the higher acidity of perfluoroalkyl sulfonic acid groups, Nafion 117 owned more efficient proton conductivity, even SPES-2 and SPES-3 had lower E_a values (9.14 and 7.51 kJ mol⁻¹, respectively). Compared to these SPESs, E_a of earlier reported sulfonated aromatic polymer were 2–4 times higher (18–30 kJ mol⁻¹) [20–24], resulting lower conductivities with similar IECs. From the vantage of conductivity, this class of sulfonated aromatic polymer is a good approach to Nafion, and is considered to be a potential candidate for PEM.

3.6. Thermal stability

In the structure of wholly aromatic backbone and side chain, these polymers own outstanding resistance to heat. As displayed in Fig. 7, both unsulfonated and sulfonated polymers show good thermal stability. The $T_{d5\%}$ of unsulfonated polymers in nitrogen were all above 480 °C, which demonstrate their excellent thermal stability. While the $T_{d5\%}$ of sulfonated polymer in nitrogen were lowered to 390 °C (shown in Table 1), due to the decomposition of sulfonic acid group at around 220 °C. They all exhibited two distinct thermal decomposition steps, which were mainly associated with the loss of the ionic groups and the degradation of the main chain, respectively.

3.7. Oxidative stability and mechanical property

The oxidative stability of the polymers was evaluated in Fenton's reagent at 80 °C. This method is regarded as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions. The weight of these SPES membranes was still retained above 86% after treatment in Fenton's reagent at 80 °C for 2 h, and they were not dissolved within 8 h.

Before tensile measurement, the membranes were immersed in water for 48 h. And their detailed data of mechanical property are listed in Table 2. The tensile strengths of the membranes were in the range of 15.5–41.2 MPa and the elongation at break of the

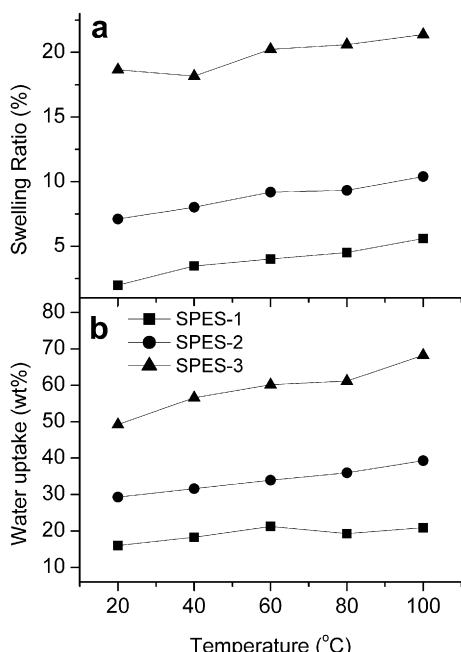
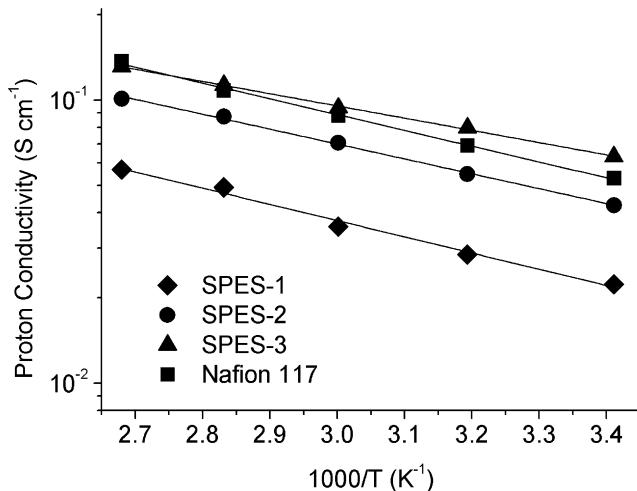


Fig. 5. (a) The swelling ratio in-plane direction and (b) water uptake dependence of temperature in water.

Table 2

Water behavior and mechanical properties of membranes.

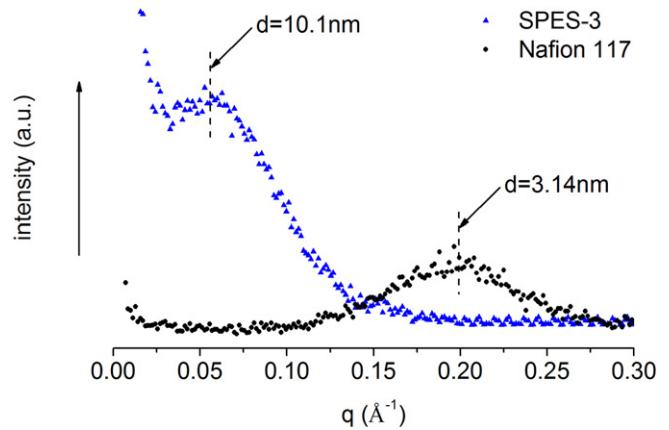
Sample	20 °C ^a			100 °C ^a			Tensile strength (MPa)	Maximum elongation (%)
	WU (%) ^b	Swelling ratio (%)	λ	WU (%) ^b	Swelling ratio (%)	λ		
SPES-1	16.0	1.9	9.9	20.9	5.6	12.9	41.2	28.3
SPES-2	29.3	7.1	12.8	39.3	10.4	17.2	23.8	33.8
SPES-3	49.2	18.7	18.1	68.3	21.4	25.1	15.5	60.9
Nafion 117	19.2	13.1	11.9	33.0	23.1	20.4	27	220

^a Measured under fully hydrated state (in water).^b Water uptake.**Fig. 6.** Proton conductivity of membranes under fully hydrated state (in water) as a function of temperature.

membranes was ranged from 28.3% to 60.9%. With the increasing of ionic group content, the membrane displays a higher elongation at break. On the other side, the tensile strength show a dramatic decrease. Overall, they owned suitable mechanical properties.

3.8. Morphological analysis

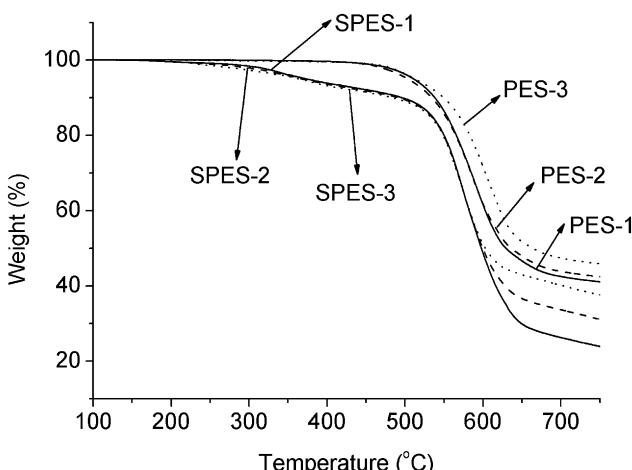
SAXS was performed to observe the internal structure of the membranes. Before test, the membranes were immersed in a 0.5 M solution of lead acetate to selectively stain the ionomer domains for SAXS. The profiles of SPES-3 and Nafion are displayed

**Fig. 8.** SAXS profiles of SPES-3 and Nafion.

in Fig. 8. Apparently, the ionic domains of SPES-3 occupy more space for its larger d value. As Jannasch reported earlier [25], the similarities of the SAXS profile of SPES-3 and Nafion 117 indicated that a high local concentration of sulfonic acid groups, and their separation from the polymer main chain, promoted a high degree of phase segregation. This is more or less consistent with conductivity measurement, although lower acidity of SPES-3 results in slightly lower conductivity compared with Nafion. The concentrated sulfonate acid groups seem aggregate greatly to form hydrophilic moiety as we expected, which serve as proton transport channels. As a result, SPES-3 earned enhanced proton conductivity.

4. Conclusions

A series of new PES based on a novel monomer were synthesized successfully. Treated with postsulfonation, SPES membranes were obtained eventually by solvent casting. Although these random copolymers own less organized structure compared with block copolymers, they exhibit considerable properties in conductivity and water behavior. Particularly, SPES-3 (IEC = 1.66 mequiv g⁻¹) maintained higher proton conductivity than Nafion at all tested temperatures. Compared with other sulfonated random PES, these SPESs show better water management. It's believed that interconnected and wide hydrophilic domains are formed, which facilitate the transport of hydronium resulting in higher conductivity. Additional, as SAXS profiles shown, distinct phase separation occurs in SPESs between hydrophilic and hydrophobic moiety. And this phase separation enhances the formation of water channels. It appears that the unique polymer structure brought by concentrated sulfonic acid groups is responsible for higher proton conductivity and excellent water behavior. Further, we will introduce several organized structures in SPES to implement superior performance in PEM applications.

**Fig. 7.** TGA curves of PESs and SPESs in N₂.

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